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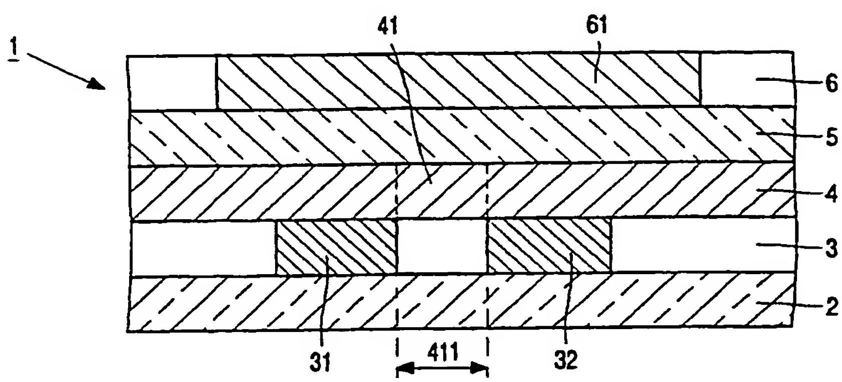
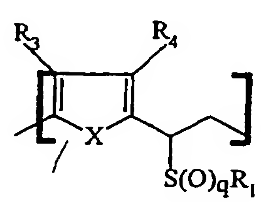
(54) Title: POLYMERS CONTAINING HETEROCYCLIC GROUPS, METHOD OF PREPARING, USE THEREOF AS A LAYER AND HETEROCYCLIC COMPOUNDS




(V)

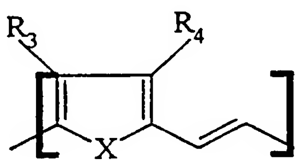
(57) Abstract: The invention provides an easy method of preparing polythienylene-vinylene and related compounds containing heterocyclic groups in the polymer chain, which compounds have improved structural and electrical properties. The method includes the reaction of a 2,5-bishalomethyl-subsituted heterocyclic compound with a thiol, a subsequent oxidation and polymerization to a novel precursor polymer comprising structural units of formula (V). Thermal elimination leads to the polythienylene-vinylene, which can be applied in the form of a layer to a substrate and used as a semiconductor material in a transistor.

WO 01/18090 A1

POLYMERS CONTAINING HETEROCYCLIC GROUPS, METHOD OF PREPARING, USE THEREOF AS A LAYER AND HETEROCYCLIC COMPOUNDS

Method of preparing a polymer containing heterocyclic groups and a layer of such a polymer on a substrate, heterocyclic compounds, polymers with heterocyclic groups in the chain and a transistor with a layer of a polymer.

The invention relates to a method of preparing a polymer containing heterocyclic groups, which polymer predominantly comprises structural units of formula (I),



(I)

wherein:

- X is selected from the group formed by an oxygen atom and a sulphur atom and a $N(R_2)$ group, wherein $R_2$ is selected from the group formed by a hydrogen atom and an alkyl group, aryl group, alkyl-aryl group and aryl-alkyl group, and
- $R_3$ and $R_4$ may be equal and are selected from the group formed by a hydrogen atom, chlorine atom, bromium atom, fluorine atom and iodide atom, and from a $C_1$-$C_4$ alkyl group, a carbonitrile group, trihalomethyl group, hydroxy group, nitro group, amino group, carboxyl group, sulphoxyl group, sulphonate group and carbonate group and from a substituted and an unsubstituted phenyl group, alkyl-aryl group and aryl-alkyl group, alkoxy group and thioalkoxy group.

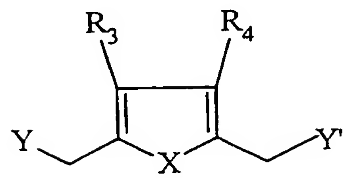
The invention further relates to heterocyclic compounds and polymers with heterocyclic groups in the chain.

The invention also relates to a method of manufacturing a layer from such a polymer.

The invention finally relates to a transistor comprising a semiconductive layer of such a polymer.

Such a method of preparing a polymer of formula I of the formula sheet is known from EP-A-0182548. An example of such a polymer is unsubstituted polythienylene-vinylene. This is the polymer of formula I wherein $R_3$ and $R_4$ are a hydrogen atom (H) and X is a sulphur atom (S), which will hereinafter also be referred to as PTV. This polymer can be used as a semiconductive material in a transistor.

The starting substance is a compound of formula II,



(II)

wherein:

- X, $R_3$ and $R_4$ have the same meaning as in formula I; and
- Y and Y' are each selected from the group formed by a chlorine atom, a bromium atom, a fluorine atom and an iodide atom and from a p-toluene sulphoxyl group and a halogen-substituted methyl sulphoxyl group.

This starting substance reacts in known manner with an excess of thioether to form a sulfonium salt, for example 2,5-bis (methyl diethyl sulfonium bromide)thiophene. This salt is used as a monomer in the polymerization step, which yields a precursor polymer with a sulfonium salt as the side group at the chain of the polymer. Finally, by means of thermal elimination, a polymer of formula I is obtained.

A drawback of this method resides in that a transistor wherein the polymer formed, in particular PTV, is used as a semiconductor material has a poor "on-off ratio" of electric current. This ratio is an impediment to the use of the transistor as a switch. The ratio means that many of the current-carrying electrons in the polymer do not contribute to the transmission of current. This limited contribution can be attributed to the absence of an ordering or crystalline structure in the polymer and the large degree of branching of the molecules of the polymer formed in this method.

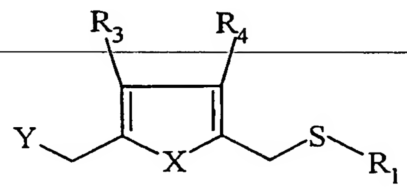
Further drawbacks of the method are the labor-intensiveness, the poor reproducibility and the low yield. In addition, the polymerization step following filtration must be carried out in a strongly diluted solution. These drawbacks substantially hamper the scaling-up of the reaction to an industrial scale.

It is an object of the invention to provide a method of preparing a polymer of formula I, in particular PTV, which method can be carried out more readily than the known

method and yields a polymer of formula I or a similar polymer with a substantially linear chain.

In the method in accordance with the invention, this object is achieved by the following steps:

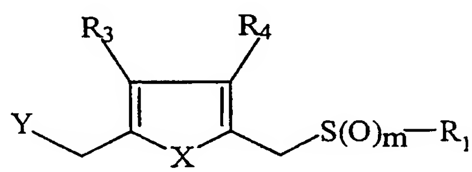
- a reaction of the compound of formula II with a thiol $R_1SH$ to form an intermediate product of formula III,



(III)

wherein:

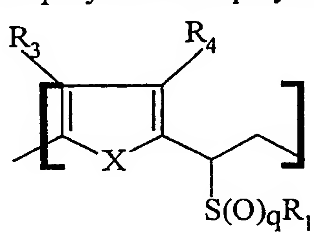
- $R_1$ is selected from the group formed by a substituted and an unsubstituted alkyl group, aryl group, alkyl-aryl group and aryl-alkyl group;
- X, Y, $R_3$ and $R_4$ have the same meaning as in formula II;
- oxidation of at least a fraction of the intermediate product to a monomer or a mixture of monomers of formula IV,



(IV)

wherein $R_1$, $R_3$, $R_4$, X and Y have the same meaning as in formula III, and wherein m is equal to 1 or 2;

- polymerization of the monomer or of a mixture of monomers of formula IV or of a mixture of monomers of formula IV and the intermediate product of formula III to form a precursor homopolymer or copolymer comprising structural units of formula V,



(V)

wherein

- X, $R_1$, $R_3$ and $R_4$ have the same meaning as in formula III;
- q is either 0, 1 or 2, but in at least a fraction of the units, q is 1 or 2;
- conversion of the precursor polymer with structural units of formula V into a polymer comprising as structural units, predominantly, the units of formula I which are obtained by elimination of the $S(O)_qR_1$ group.

The method comprises a reaction step, an oxidation step, a polymerization step and an elimination step. In the reaction step of the method, the reaction of the starting substance with a thiol leads to the formation of a thioether as the intermediate product. In the oxidation step, the intermediate product is partly or completely oxidized to a compound of formula IV, which comprises a sulphinyl group or a sulphonyl group, or to a mixture of these compounds. In addition to a peracid, such as m-chloroperbenzoic acid, inter alia hydrogen peroxide and tellurium oxide may be used as the oxidation agent. A first advantage of this method resides in that the intermediate product of formula V is not charged. As a result, this product is less sensitive to the occurrence of undesirable side reactions, as compared to the sulfonium ion in accordance with the state of the art. Also the reaction step can be readily carried out. In addition, it is favorable that, for each molecule of the starting substance of formula II, predominantly only one substitution of a group Y or Y' by $R_1S$ takes place. It has been recognized that the remaining Y group in the polymerization step can be used as a leaving group. In addition, it is assumed that by substitution of a single group Y per molecule, undesirable polymerization reactions between $R_1S$ groups are precluded. The result is an at least substantially linear polymer.

The polymerization step to form a polymer comprising structural units of formula V takes place by the addition of a base. The base can be added to a composition, either a solution or a fine dispersion, of a formula IV-monomer obtained in the oxidation step. This monomer may be single-oxidized (m = 1) or double-oxidized (m = 2). In this first case, a homopolymer is formed comprising substantially structural units of formula V with q = 1 or q = 2. The base can also be added to a mixture of the monomers. In this second case, a copolymer is formed which comprises structural units of formula V with q = 1 and units with q = 2. The base can further be added to a mixture of at least one of the monomers and the intermediate product. In this third case, a copolymer is formed which comprises structural units of formula V with q = 0, units with q = 1 and, possibly, units with q = 2. The base can additionally be added to a mixture of compounds of formula IV and possibly formula III, which compounds have been independently obtained. In this fourth case, a copolymer is formed comprising structural units of formula V, which units may differ from each other as

regards the $R_1$, $R_3$, $R_4$, and X-group and the value of q. Another method of preparing a copolymer comprising structural units of formula V with q = 1 and q = 2, is a partial oxidation of the precursor homopolymer of formula V with structural units q = 1.

The method in accordance with the invention is also based on the recognition that the hydrogen atoms at the carbon atom between the sulphur atom and the heterocyclic ring are acid. As a result, proton transfer from the monomer to the base is easy. It is assumed that the halogen atom splits off from this deprotonated monomer in the form of a halogenide ion, whereafter the actual polymerization takes place. Presumably, this polymerization takes place via a radical mechanism. To preclude that the base carries out a substitution at the location of the halogen atom, the choice of a non-nucleophilic base is desirable. An example of such a base is tert-butyloxide. Another example is a tertiary amine. The precursor homopolymer or copolymer is converted, in the elimination step, into a polymer by means of heat, which polymer predominantly comprises structural units of formula I.

In embodiments of the method in accordance with the invention, an aromatic and a $C_1$ to $C_{10}$ aliphatic thiol are selected as the thiol $R_1SH$. The $R_1$ group may be branched and substituted. Substituents are, inter alia, halogen, amino, nitro, hydroxy, alkoxy, carbonate and sulphonate groups. The choice of the thiol $R_1SH$ appears to be non-critical relative to one or more steps in the method according to the invention. This is based on the assumption that substitutions in the $R_1$ group on a $\beta$, $\gamma$ or further atom with respect to the sulphur atom, do not cause interaction between the sulphur atom and the substituent.

This variety of thiols $R_1SH$ enables a thiol to be chosen which has favorable side effects. Examples of such effects are the solubility of intermediate products and monomers in a solvent such as water or alcohol; the stability of the precursor monomer's group $S(O)_mR_1$ to be eliminated, where m is equal to 1 or 2 and not necessarily the same for all groups within a precursor polymer; the volatility of the group $S(O)_mR_1$ or reaction products thereof in a vacuum, in a nitrogen atmosphere and in air; and the use of the group $S(O)_mR_1$ as an additive in the polymer formed. The example of the solubility in water seems to be practicable by choosing a $R_1$ group which is substituted with one or more polar groups as hydroxy and amino groups.

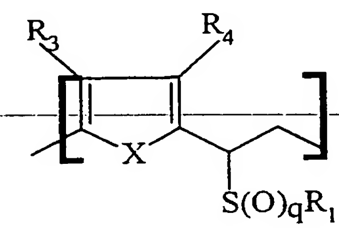
The method in accordance with the invention leads to novel heterocyclic compounds of formula VI and precursor polymers with heterocyclic groups in the chain, which groups are structural units of formula V. The method in accordance with the invention additionally leads to novel copolymers comprising, as structural units, the units of formulae I and VII. Such a polymer apparently has the advantage that it is less sensitive to oxygen

absorption. Supposedly, an absorbed oxygen molecule links to a conjugated chain, causing the conduction in the chain to be annihilated. In comparison with a polymer which predominantly comprises units of formula I, the copolymer has more, yet smaller, conjugated chain parts. As a result of the larger number of conjugated chain parts, the relative influence of the linkage of one oxygen molecule is smaller. This causes the stability of the conductance of the polymer to be increased.

A further object of the invention is to provide a method of manufacturing a layer of a polymer as described in the opening paragraph, which method can be readily carried out.

This object of the invention is achieved in a method comprising:

- the provision, on a substrate, of a layer of a precursor polymer which predominantly comprises structural units of formula V



(V)

wherein:

- $R_1$ is selected from the group formed by a substituted and an unsubstituted alkyl, aryl, alkyl aryl and aryl alkyl group;
- q is selected from the group formed by 0, 1 and 2 but is equal, in at least one fraction of the units, to 1 or 2;
- X, $R_3$ and $R_4$ have the same meaning as in formula I;

the conversion of the precursor polymer applied in the form of a layer to a polymer which predominantly comprises structural units of formula I by applying heat.

This method in accordance with the invention can be readily carried out because the precursor polymers with structural units of formula V can be readily dissolved in solvents such as tetrahydrofuran and chlorinated hydrocarbons. As a result of said solubility, the necessary amount of solvents can be reduced and a filtration step omitted. In addition, HCl gas does not have to be used in the elimination step. In the method known from an article by H. Murata et. al., *Synthetic metals* 36 (1990), 95-102, wherein a precursor polymer with alkoxy and hydroxy side groups is employed, HCl gas must be used.

Layers manufactured by means of the method in accordance with the invention have the additional advantage that they possess excellent electrical properties. A transistor in

which the PTV layer formed by means of the method is used as a semiconductor has a high on-off ratio of electric current. At the same time, the mobility of electric charge under the influence of an electric field, i.e. the mobility, is at least equally high as the mobility of a layer of PTV formed by means of the method proposed by Murata et. al. In addition, this precursor polymer, and probably also the PTV, are largely unbranched. This can be attributed to the satisfactory solubility of the precursor polymer. Probably, similar polymers in accordance with the invention comprising pyrrole groups or furan groups possess similar properties. The reason for this being that these polymers too are largely unbranched and, according to Brown et. al., *Synthetic metals* 88 (1997), 48, the mechanism of movement of electric charge is independent of the heterocyclic atom in the chain of the polymer.

A substrate obtained using the method in accordance with the invention, which comprises a layer of a polymer with structural units of formula I, can be used as a semiconductor in a transistor. A transistor comprising such a semiconductor has a high "on-off" ratio. The use of a layer of such a polymer, in particular PTV, is favorable as compared to other semiconductors owing to the "stack integrity". This means that the layer can be used as a substrate for a subsequent layer. Such a transistor may form part of an integrated circuit and can be used therein, inter alia, as a switch or a memory unit.

These and other aspects of the method of preparing a polymer comprising structural units of formula I, and of the method of preparing a layer of such a polymer, heterocyclic compounds of formulae III and IV, polymers containing structural units of formula V, and the transistor in accordance with the invention will be described in greater detail hereinafter with reference to the drawings.

In the drawings:

Fig. 1 is a diagrammatic, cross-sectional view of a transistor;

Fig. 2 is a diagram of the current through a transistor comprising a semiconductive PTV layer prepared by means of the method in accordance with the invention, as a function of the voltage applied at the gate electrode;

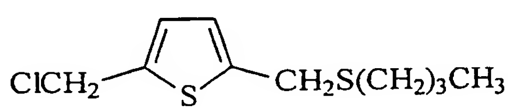
Fig. 3 is a diagram of the mobility in a transistor comprising a semiconductive PTV layer prepared in accordance with the method of the invention, as a function of the voltage applied at the gate electrode.

Fig. 4 shows a reaction scheme of the polymerization step of a method in accordance with the invention.

Example 1: synthesis of 2-butylsulphinylmethyl-5-chloromethylthiophene

The monomer 2-butylsulphinylmethyl-5-chloromethylthiophene is a compound of formula IV, wherein Y = $ClCH_2$, X = S, $R_1 = C_4H_9$, $R_3$ = H, $R_4$ = H and m = 1. This monomer is synthesized in two steps: the reaction step and the oxidation step.

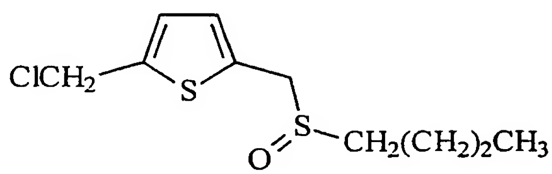
In the reaction step, sodium hydroxide tablets (14.0 g, 0.35 mol) are added to an ice-cooled mixture of 2,5-(bischloromethyl)thiophene (68.6 g, 0.379 mol, distilled material from the chloromethylation of thiophene, not entirely pure) and n-butanethiol (36 ml, 0.336 mol) in 175 ml. The mixture is stirred overnight, whereby the temperature rises to room temperature. Subsequently, the mixture is heated to 50-60 °C for a number of hours, while stirring sufficiently. The remaining thiol is evaporated. The residue is treated with hexane/toluene and water, leading to the formation of two layers. The layers are separated. The organic layer is washed with water. This layer is subsequently dried. The solvent is evaporated. The residue is distilled, yielding first of all residual starting substance, subsequently a side product and then, at approximately 130 °C/0.01 mbar, a product of 2-butylthiomethyl-5-chloromethylthiophene. The structural formula of this product is shown in formula VIII. Results of proton-NMR in $CCl_4$ are : $\delta$ = 3.75 (s, 2H), 4.65 (s, 2H), 6.5-6.9 (m, 2H).




(VIII)

In the oxidation step, m-chloroperbenzoic acid (m-CPBA, 40 g 70%, 0.16 mol) is added in small quantities to a cold solution of the product of formula VIII (37.6 g 0.16 mol) in 200 ml dichloromethane. The reaction is exothermal and a white suspension is formed. After removal of the cooling bath and stirring for one hour, the reaction mixture is added to diluted sodium hydroxide solution. Layers are formed, which are subsequently separated from each other. The organic layer is washed with water and dried. The organic solvent is evaporated. The residue is purified by column chromatography wherein use is made of silica and, as an eluent, a mixture of hexane and ethylacetate. The product is identified with proton-NMR in $CDCl_3$:$\delta$ = 0.8 (s, 3H), 1.2-1.8 (m, 4H), 2.55 (t, 2H), 4.05

(AB, 2H), 4.65 (s, 2H), 6.8 (d, 1H), 6.95 (d, 1H). The structural formula of the product is shown in formula IX:



(IX)

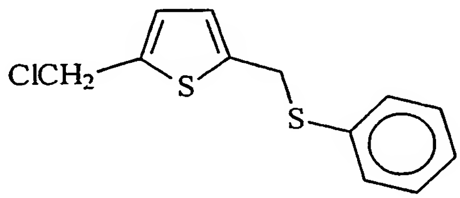
Example 2: synthesis of 2-phenylsulphinylmethyl-5-chloromethylthiophene

The monomer 2-phenylsulphinylmethyl-5-chloromethylthiophene is a compound of formula IV, wherein Y = $ClCH_2$, X = S, $R_1$ = $C_6H_5$, $R_3$ = H, $R_4$ = H and m = 1. This monomer is synthesized in two steps: the reaction step and the oxidation step.

In the reaction step, sodium hydroxide tablets (14.0 g, 0.35 mol) are added to an ice-cooled mixture of 2,5-bis(chloromethyl)thiophene and 34 ml thiophenol (0.33 mol) in 175 ml. The ice bath is removed and the mixture is stirred for 12 hours, whereafter it is heated to 50-60 °C for 24 hours. Next, liquid is evaporated. The residue is dissolved in a mixture of hexane and toluene. After washing three times with water, a drying operation is carried out. The residue is stirred with a solution of toluene in hexane, leading to precipitation. The solid is filtered and washed with hexane. The hexane in the filtrate is evaporated while stirring. The filtrate is subsequently heated to 0.1 mbar to remove the 2,5-bischloromethylthiophene. The product is characterized by proton-NMR, which shows that the ratio between the groups $CH_2C_6H_5$:$CH_2Cl$ ranges from approximately 1.5 to 1. This means that approximately 0.187 mol of 2-phenylthiomethyl-5-chloromethylthiophene is formed and approximately 0.047 mol of a side product, namely 2,5-bis(phenylthiomethyl)thiophene.

Without further purification, this mixture is used in the oxidation step. The mixture is dissolved in 400 ml dichloromethane and subsequently cooled to a temperature below 10 °C. A quantity of 70 g of 70% m-CPBA (0.28 mol) is added in small quantities. The mixture is stirred for one hour, whereby the temperature rises to 7 °C. Subsequently, 250 ml of diluted sodium hydroxide solution is added. The layers formed are separated. The organic layer is washed twice with water. The layer is subsequently dried. The organic solvent is evaporated. The residue is purified, using silica and, as an eluent, a mixture of

ethylacetate and hexane. The polarity of the eluent is slowly increased by adding ethylacetate. The structural formula of the product, i.e. 2-phenylsulphinylmethyl-5-chloromethylthiophene, is shown in formula XI. The product is identified with proton-NMR:$\delta$ = 4.15 (s, 2H), 4.65 (s, 2H), 6.55 (d, 1H), 6.85 (d, 1H), 7.4 (m, 5H).



(XI)

Example 3: synthesis of a precursor polymer

A degassed solution of 1 g (3.7 mmol) 2-phenylsulphinylmethyl-5-chloromethylthiophene, i.e. a compound of formula XI, in 15 ml of a 1:5 mixture of dry sec-BuOH and THF is cooled to a temperature below –40 °C in a nitrogen atmosphere. Subsequently, 3.7 mmol potassium tert-butoxide in 10 ml THF is slowly added. A reaction takes place as shown in Fig. 4, wherein R = $C_6H_5$. After two hours, the mixture is acidified with acetic acid. Water is added and the mixture is extracted twice with chloroform. The combined organic layers are washed three times with water and are subsequently dried on magnesium sulfate. The solvent is evaporated. The resultant solid is stirred in diethylether and subsequently filtered. After drying, the substance is again dissolved in chloroform and precipitated twice in dry diethylether. A precursor polymer with structural units in accordance with formula V, wherein $R_1 = C_6H_5$, q = 1, X = S, $R_3$ = H and $R_4$ = H is obtained. The chain length n is at least 10.

Example 4: preparation of a layer of PTV, and properties of said layer

One percent by weight of the precursor polymer with structural units in accordance with formula V, wherein $R_1 = C_6H_5$, q = 1, X = S, $R_3$ = H and $R_4$ = H is dissolved in chloromethane and, without filtration, spincoated onto a standard MISFET test substrate. The spincoated substrate is heated to 150 °C in a vacuum for 10 minutes, as a result of which a vapor escapes. It is supposed that the vapor includes the compound $C_6H_5SOH$ or reaction products thereof. Subsequently, the substrate is cooled. By means of IR and UV spectrometry it is established that polythienylene-vinylene has been formed. The source-drain current

through the PTV layer is measured as a function of the "gate" voltage $V_g$ in the linear regime and in the saturation regime, whereby "drain" voltages $V_d$ of, respectively, -2 and –20 V are used. The on-off ratio is calculated of the measuring results shown in Fig. 2. This ratio is defined as the ratio of the current of a transistor in the "on" state, with $V_g = V_d < 0$ V, to the current in the "off" state, with $V_g = 0$ V, $V_d < 0$ V, with $V_g$ referring to the "gate" voltage and $V_d$ referring to the "drain" or supply voltage. The on-off ratio is found to be $10^6$, which is a high value. The mobility is calculated from the results in Fig. 2 in accordance with the formula $\mu = \mu(V_g) = (L/(ZC_iV_d))\delta I_{st}/\delta V_g$ for the limit of $V_d$ to (?) zero, wherein $\mu$ refers to the mobility, L to the channel length, Z to the channel width, $C_i$ to the capacity per unit of area of the insulator and $I_{sd}$ to the source-drain current. As shown in Fig. 3, a mobility of 0.003 has been found. A repetition of the elimination in a nitrogen atmosphere does not have a large effect on the mobility of the PTV obtained. A variation of the temperature and the duration of the elimination between 100 and 200 degrees Celsius and between 5 and 30 minutes has been found possible. Complete elimination is not attained in all cases.

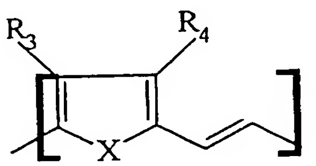
Example 5: the structure of a transistor with PTV

The transistor 1 shown in Fig. 1 comprises an electrically insulating substrate 2, which supports a first layer 3 of a polymer material, for example polyaniline, which comprises electroconductive parts and accommodates a source electrode 31 and a drain electrode 32. The electrically non-conducting parts of the first layer 3 can be removed. The organic semi-conductive layer 4 comprising polythienylene-vinylene prepared by means of the method in accordance with the invention, has a channel 41, the length of the channel being indicated by number 411. An electrically insulating layer 5, for example of polyvinylphenol, covers the layer 4 and insulates the gate electrode 61 with respect to the channel 41. The gate electrode forms part of a second conductive layer 6 which is made, for example, of doped polyaniline. The electrically non-conducting parts of this second conductive layer can be removed.

Other examples of field effect transistors include "bottom-gate" structures and transistors with other organic polymers or non-polymeric layers for the insulating and conducting parts. The transistor may form part of a larger circuit, such as an inverter, an oscillator or an integrated circuit. Apart from a field effect transistor, a bipolar transistor with a semiconductive layer of polythienylene-vinylene has been prepared in accordance with the method of the invention.

CLAIMS:

1. A method of preparing a polymer containing heterocyclic groups, which polymer predominantly comprises structural units of formula I,

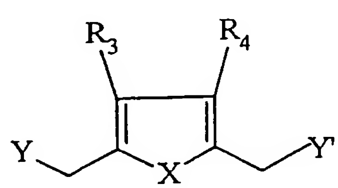


(I)

wherein:

- X is selected from the group formed by an oxygen atom and a sulphur atom and a $N(R_2)$ group, wherein $R_2$ is selected from the group formed by a hydrogen atom and an alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- $R_3$ and $R_4$ may be equal and are selected from the group formed by a hydrogen, chlorine, bromium, fluorine and iodide atom and from a $C_1$-$C_4$ alkyl, carbonitrile, trihalomethyl, hydroxy, nitro, amino, carboxyl, sulphoxyl, sulphonate and carbonate group and from a substituted and an unsubstituted phenyl, alkyl-aryl and aryl-alkyl, alkoxy and thioalkoxy group;

starting from an organic sulphur compound and a compound of formula II,



(II)

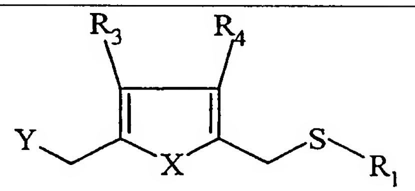
wherein:

- X, $R_3$ and $R_4$ have the same meaning as in formula I;

- Y and Y' are each selected from the group formed by a chlorine, bromium, fluorine and iodide atom and from a p-toluene sulphoxyl group and a halogen-substituted methyl sulphoxyl group;

comprising the following steps:

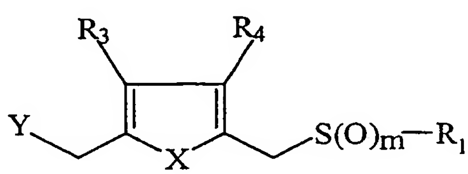
- a reaction of the compound of formula II with a thiol $R_1SH$ to form an intermediate product of formula III,



(III)

wherein:

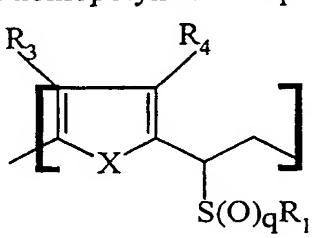
- $R_1$ is selected from the group formed by a substituted and an unsubstituted alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- X, Y, $R_3$ and $R_4$ have the same meaning as in formula II;
- oxidation of at least a fraction of the intermediate product to a monomer or a mixture of monomers of formula IV,



(IV)

wherein

- $R_1$, $R_3$, $R_4$, X and Y have the same meaning as in formula III, and wherein m is equal to 1 or 2;
- polymerization of the monomer or of a mixture of monomers of formula IV or of a mixture of monomers of formula IV and the intermediate product of formula III to form a precursor homopolymer or copolymer comprising structural units of formula V,



(V)

wherein

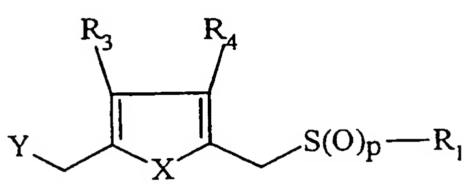
- X, $R_1$, $R_3$ and $R_4$ have the same meaning as in formula III;
- q is either 0, 1 or 2, but in at least a fraction of the units, q is 1 or 2;
- conversion of the precursor polymer with structural units of formula V into a polymer comprising as structural units, predominantly, the units of formula I which are obtained by elimination of the $S(O)_qR_1$ group.

2. A method as claimed in claim 1, characterized in that a $C_1$ to $C_{10}$ alkyl thiol is used as the thiol $R_1SH$.

3. A method as claimed in claim 1, characterized in that a phenyl thiol is used as the thiol $R_1SH$.

4. A method as claimed in claim 1, characterized in that q is equal to 1 or 2 for substantially all units of formula V.

5. Heterocyclic compounds of formula VI,



(VI)

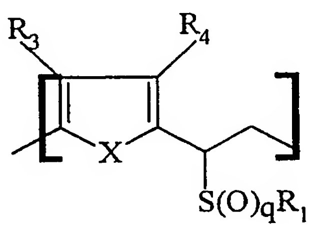
wherein:

- $R_1$ is selected from the group formed by a substituted and an unsubstituted alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- X is selected from the group formed by a $N(R_2)$ group and a sulphur atom and an oxygen atom, wherein $R_2$ is selected from the group formed by a hydrogen atom and an alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- Y is selected from the group formed by a chlorine, bromium, fluorine and iodide atom and from a p-toluene sulphoxyl group and a halogen-substituted methyl sulphoxyl group;
- $R_3$ and $R_4$ may be equal and are selected from the group formed by a hydrogen, chlorine, bromium, fluorine and iodide atom, and from a hydroxy, nitro, amino, carboxyl,

sulphoxyl, sulphonate and carbonate group and from a substituted and an unsubstituted alkyl, aryl, alkyl-aryl and aryl-alkyl group;

- p is equal to 0, 1 or 2.

6. Polymers with heterocyclic groups in the chain, characterized in that the groups are structural units of formula V,



(V)

wherein:

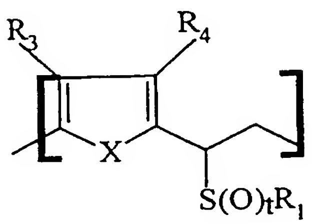
- $R_1$ is selected from the group formed by a substituted and an unsubstituted alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- X is selected from the group formed by an oxygen atom and a sulphur atom and an $N(R_2)$group, wherein $R_2$ is selected from the group formed by a hydrogen atom and an alkyl, aryl, alkyl-aryl or aryl-alkyl group;
- $R_3$ and $R_4$ are selected from the group formed by a hydrogen, chlorine, bromium, fluorine and iodide atom, and from a hydroxy, nitro, amino, carboxyl, sulphoxyl, sulphonate and carbonate group, and from a substituted and an unsubstituted alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- q is either 0, 1 or 2, but, in at least a fraction of the units, q is 1 or 2.

7. Polymers as claimed in claim 6, characterized in that

- X is a sulphur atom;
- $R_3$ and $R_4$ are hydrogen atoms.

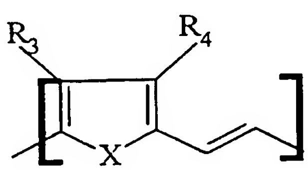
8. Polymers as claimed in claim 7, characterized in that, in substantially all units, q is 1 or 2.

9. Polymers whose chain predominantly comprises structural units of formula VII



(VII)

and of formula I



(I)

in which units:

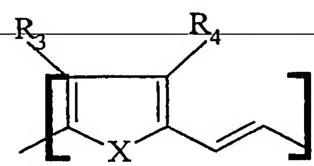
- $R_1$ is selected from the group formed by a substituted and an unsubstituted alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- X is selected from the group formed by a $N(R_2)$ group, an oxygen atom and a sulphur atom, wherein $R_2$ is selected from the group formed by a hydrogen atom and an alkyl, aryl, alkyl-aryl or aryl-alkyl group;
- $R_3$ and $R_4$ are selected from the group formed by a hydrogen, chlorine, bromium, fluorine and iodide atom, and from a hydroxy, nitro, amino, carboxyl, sulphoxyl, sulphonate and carbonate group and from a substituted and an unsubstituted alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- X, $R_1$, $R_3$ and $R_4$ have equal or different meanings for units of formula VII;
- X, $R_3$, $R_4$ have equal or different meanings for units of formula I;
- t has an equal or different meaning, selected from the group consisting of 0 and 1, for units of formula VII.

10. Polymers as claimed in claim 9, wherein the number of structural units of formula I is larger than the number of structural units of formula VII.

11. Polymers as claimed in claim 9 or 10, wherein:

- X is a sulphur atom;
- $R_3$ and $R_4$ are hydrogen atoms;
- t is equal to 1.

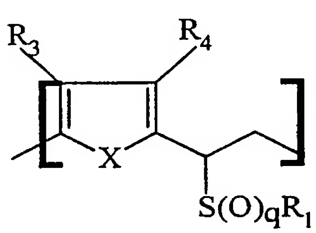
12. Method of manufacturing a layer of a polymer comprising predominantly the structural units of formula I on a substrate,



(I)

wherein:
- X is selected from the group formed by an oxygen atom and a sulphur atom and a $N(R_2)$ group, wherein $R_2$ is selected from the group formed by a hydrogen atom and an alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- $R_3$ and $R_4$ are selected from the group formed by a hydrogen, chlorine, bromium, fluorine and iodide atom, from a $C_1$ to $C_4$ alkyl, from a carbonitrile, trihalomethyl, hydroxy, nitro, amino, carboxyl, sulphoxyl, sulphonate and carbonate group and from a substituted and an unsubstituted phenyl, alkyl-aryl and aryl-alkyl, alkoxy and thioalkoxy group;

which method comprises the following steps:
- the provision, on a substrate, of a layer of a precursor polymer which predominantly comprises structural units of formula V

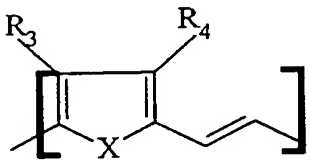


(V)

wherein:
- $R_1$ is selected from the group formed by a substituted and an unsubstituted alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- q is either 0, 1 and 2 but, in at least a fraction of the units, q is 1 or 2;

- X, $R_3$ and $R_4$ have the same meaning as in formula I;
- the conversion of the precursor polymer applied in the form of a layer into a polymer which predominantly comprises structural units of formula I by heating.

13. A transistor comprising a layer of a polymer which predominantly comprises structural units of formula I,

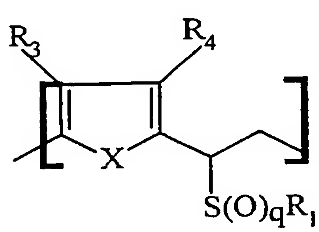


(I)

wherein:

- X is selected from the group formed by a $N(R_2)$ group, an oxygen atom and a sulphur atom, wherein $R_2$ is selected from the group formed by a hydrogen atom and an alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- $R_3$ and $R_4$ are selected from the group formed by a hydrogen, chlorine, bromium, fluorine and iodide atom, and from a hydroxy, nitro, amino, carboxyl, sulphoxyl, sulphonate and carbonate group, and from a substituted and an unsubstituted alkyl, aryl, alkyl-aryl and aryl-alkyl group;

wherein the polymer is prepared from a precursor polymer which predominantly comprises structural units of formula V



(V)

wherein:

- $R_1$ is selected from the group formed by a substituted and an unsubstituted alkyl, aryl, alkyl-aryl and aryl-alkyl group;
- X, $R_3$ and $R_4$ have the same meaning as in formula I;
- q is either 0, 1 or 2, but, in at least a fraction of the units, q is 1 or 2.

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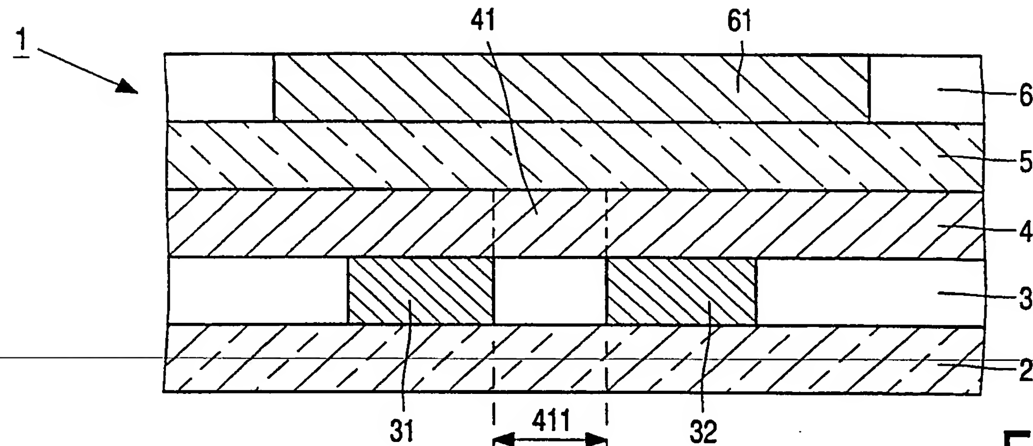


FIG. 1

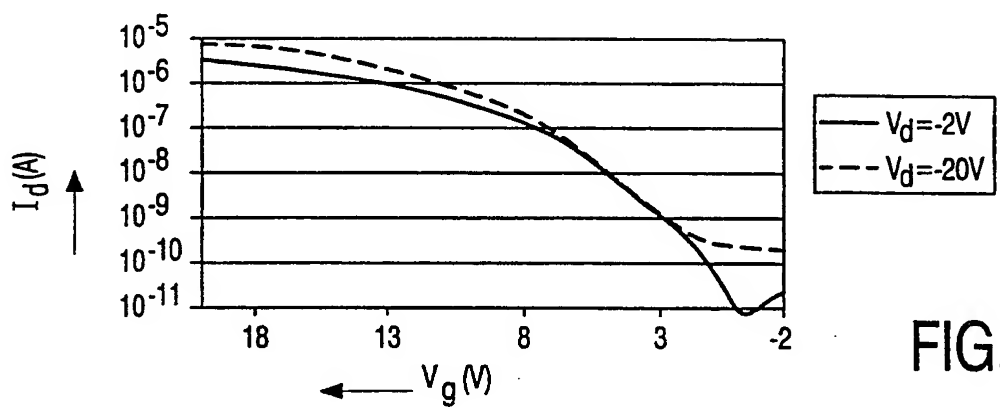


FIG. 2

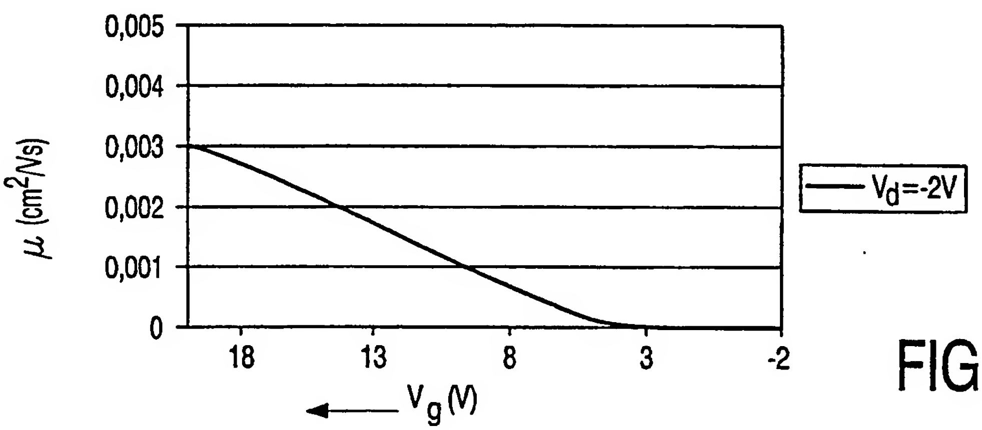


FIG. 3

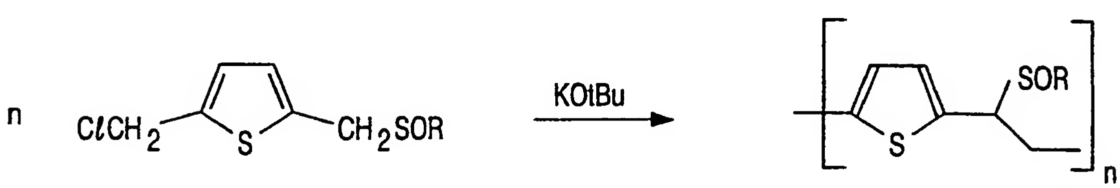


FIG. 4

# INTERNATIONAL SEARCH REPORT

Inter. ...onal Application No
PCT/EP 00/07971

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G61/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| A | column 11, line 31 - line 64 | 1-13 |
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 14 December 2000 | 08/01/2001 |

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| European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | Paalman, R |

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# INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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PCT/EP 00/07971

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